CORE
Metadata, citation and similar papers at core.ac.uk
Provided by EKE Repository of Publications

Acta Acad. Paed. Agriensis, Sectio Pericemonologica **XXX** *(2006) 89–95*

Investigation of the interaction of pesticides with different soil samples

Cs. Csutoras – A. Kiss

Department of Chemistry – Department of Biochemistry

Abstract: The interaction of atrazine, simazine, terbutryn, prometryn, diuron and sandy as well as brown forest soil samples from different layers was investigated. A suitable, simple model was created, similarly to column chromatography. Polar or apolar character of the pesticides was proven to be the most important factor in the soil-pesticide interaction, increasing polarity resulted in enhanced bond strength between the soil and pesticide.

1. Introduction

Pesticide degradation, or the breakdown of pesticides is a beneficial process. The reactions that destroy pesticides, change most pesticide residues in the environment generally to inactive, less toxic and harmless compounds, but sometimes degradation can lead to the formation of more toxic compounds compared to the original pesticides. Degradation is also detrimental, when a pesticide is destroyed before the target pest has been controlled.

Several data can be found in the literature on revealing the microbial, chemical and photodegradation processes [1, 2, 3].

The persistence and degradation of various pesticides were thoroughly investigated during composting [1, 2]. Most microbiological degradation of pesticides occurs in the soil, thus soil conditions affect the rate of degradation because of their direct influence on microbial growth and activity [3, 4].

Photochemical degradation of pesticides is the breakdown of pesticides by light, particularly sunlight. Photodegradation can destroy pesticides on foliage, on the soil surface and even in the air. Photochemical degradation of pesticides can be applied for the decontamination of natural water or contaminated soils [5, 6]. Two methods were suggested for the acceleration of the oxidation of organic contaminants (e.g. pesticides) of water, acceleration by oxidants and photo-enhancement by dyes [7].

The soil adsorption behaviour of atrazine and its photodegradation products was thoroughly investigated in the case of brown soil samples. Their photomineralization using titanium dioxide catalyst was elaborated [8, 9, 10]. Behaviour of other s-triazine residues in groundwater was also widely investigated [11, 12].

An important aim of environmental chemists is revealing of the interactions of pesticides and soils. Leaching and degradation of pesticides of different type in sandy soil were studied by Kookana et. al. and elsewhere [13]. Di et. al. suggested a method for the determination of groundwater contamination potential of pesticides, in which the degradation rate of pesticides in both the surface and subsurface soils is an important factor [14]. Pesticide degradation in soil was investigated in the case of several pesticides (for example atrazine) [15].

The adsorption process binds pesticides to soil particles. One problem resulting from pesticide adsorption can be reduced pest control. For example, weeds may not be controlled if a herbicide is held tightly to soil particles and cannot be taken up by the roots of the target weeds. Plant injury can be another problem resulting from adsorption of pesticides to soil particles. Injury may occur when a pesticide used for one crop is later released from the soil particles in amounts great enough to cause injury to a sensitive rotational crop. This pesticide carry-over can also lead to the presence of illegal residues on rotational food or feed crops.

While adsorption is particularly important and our research group has investigated recently thoroughly the photodegradation of various pesticides [16, 17], we decided in this paper to reveal the adsorption process of atrazine, simazine, prometryn, terbutryn and diuron and some photodegradation products.

2. Materials and Methods

2.1. Characterization of soils used in the experiments:

Two types of soils were chosen for the experiments, sandy soil and brown forest soil. 3 layers were examined, plough layer (0-20cm), and two subsoil layers (20-100cm and 100-200cm). Both type of soil samples were characterized using traditional methods, measuring for example pH, specific conductivity and humus content.

2.2. Preparation of chromatographic columns for the experiments:

Soil samples, taken from different layers were dried at room temperature, for 10 days. After dry crushing, soils were sieved through a 0.4 μm sieve, to achieve approximately equal particle size. A chromatographic col-

umn was filled with this fine powder (50g) after moistening with chloroform. The pesticide (0.1mmol) was eluted with chloroform during the experiments, and thin layer chromatography was applied to follow the elution process. The pesticide after the elution process was identified by GC-MS technique.

2.3. Identification of pesticides and their degradation products

The examined pesticides (higher than 99% HPLC purity) and other applied chemicals were purchased from Aldrich. Thin layer chromatography was performed on precoated Merck 5554 Kieselgel 60 F_{254} foils using a 9:1 chloroform – methanol developing system. Pesticides were identified by using GC-MS technique. The GC separations and the mass spectrometric measurements were performed by using a Perkin ELMER Auto System XL Gaschromatograph and a Turbo Mass Spectrometer under the next measuring conditions: HP-Ultra 2 (25m X 0.32 mm X 0,52 μm) column, 280 °C injector temperature, carrier gas He (2 ml/min). Temperature programme: t_1=60 °C (2 min isotherm), 32 °C/min (8 min isotherm), Perkin Elmer Turbo Mass detector, EI (70 eV) ionization mode, 1s/dekade scan time, 290 °C interface temperature, 220 °C ionsource temperature, 1 μl inject volume, 1/10 split. The structure identifications based on the interpretation of the fragmentation pathways.

3. Results and Discussion

In this paper we focus on revealing the adsorption process of atrazine, simazine, prometryn, terbutryn and diuron and some photodegradation products (Figure 1).

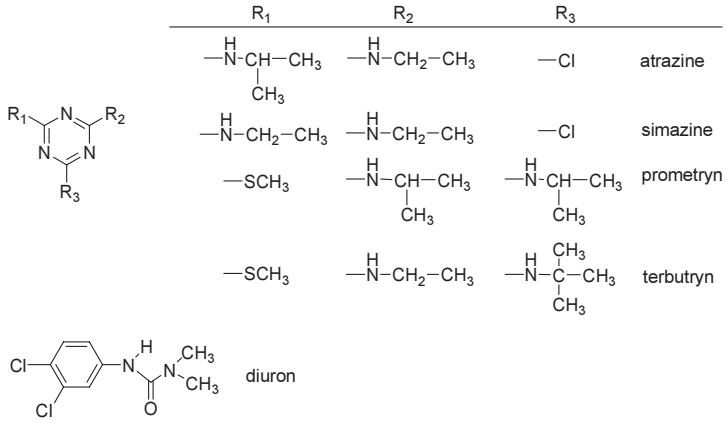

Figure 1. Chemical structures of examined pesticides

Table 1. Characterization of soil samples

Soil type	**Layer**	**pH**	**Humus-content** (%)	**Spec. conductivity (µs/cm)**	**Ca^{2+} (mg in 100g soil)**	**$CaCO_3$ (%)**	**Total petroleum hydrocarbon (mg/kg)**
Sandy	0-20 cm	5.48	1.58	96	18	5-10	<5
Sandy	50-100 cm	5.54	1.30	92	17	2-5	<5
Sandy	150-200 cm	5.27	0.74	35	12	2-5	<5
Brown	0-20 cm	7.26	2.32	111	5380	10-15	<10
Brown	50-100 cm	6.55	1.24	110	4120	10-15	<10
Brown	150-200 cm	6.62	0.62	95	4080	10-15	<10

Both sandy and brown forest soil samples were characterized. The results of the characterization of soil samples are summarized in table 1.

A simple model was created for the investigation of the pesticide-soil interactions, pesticide adsorption, pesticide transfer and leaching processes. The modelling equipment was built similarly to column chromatography. The column was filled with the appropriately prepared soil sample. To avoid the effect of water on adsorption, the experiments were carried out under dry conditions and chloroform was used as eluent. According to general experiences moisture affects adsorption, wet soils tend to adsorb less pesticide than dry soils because water molecules compete with the pesticide for the binding sites. The bond strength between soil and pesticide was measured in a very simple way. Retention time or the amount of eluent, that is necessary to wash off the pesticide, can deliver precise data on the bond strength between the pesticide and soil. The results of the column chromatographic experiments are shown in table 2.

Table 2. Pesticides, soil layers and amount of eluent (mL ± 3%)

Soil type	Pesticide	Soil layers (cm)		
		0-20	50-100	150-200
sandy	terbutryn	15.5	17.5	21
sandy	prometryn	16	18	23
sandy	atrazine	17.5	18.5	23
sandy	simazine	18	19.5	24.5
sandy	diuron	18.5	21.5	26.5
brown	terbutryn	24.5	28	64
brown	prometryn	26	28.5	65.5
brown	atrazine	26.5	31	72
brown	simazine	27.5	31.5	74
brown	diuron	31	38.5	83.5

According to our results, in the case of sandy soil the bond strength between the soil and pesticide is significantly lower, compared with the findings in the case of brown forest soil. It can be explained by difference of soil structure and composition of soil particles. Adsorption mostly occurs because of the attraction between the chemical and soil particles. Positively charged pesticide molecules for example, are attracted and bond to negatively charged clay particles. In the case of both soil types our results show, that the adsorption of pesticides in subsoil layers is gradually higher compared with plough layer. In accordance with our expectations s-triazine type pesticides (terbutryn, prometryn, atrazine, simazine) have similar adsorption properties. The little differences are connected to the polar or apolar character of the examined pesticide. The least polar terbutryn shows in both soil types less bond strength than the other examined pesticides, including the most polar diuron, which shows the highest bond strength to sandy and brown forest soils. The „relative adsorption values" were calculated using the values from the above tables for better representation. Using these values, the comparison of the adsorption of different pesticides can be more efficient and precise. The comparison of the relative adsorption values are shown in figure 2.

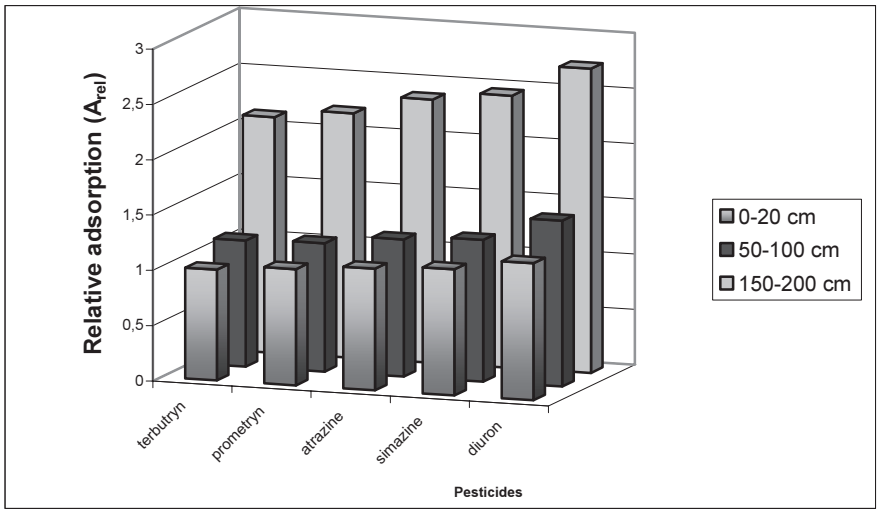

Figure 2. Relative adsorption values of the examined pesticides
**Relative adsorption values were calculated according to the following equation: $A_{rel.}$ = (The amount of eluent in sandy soil + the amount of eluent in brown forest soil)/40 (In the case of terbutryn in plough layer (0–20cm) $A_{rel.}$=1).*

Our experiments were extended to the investigation of the interaction of the photodegradation products of atrazine and prometryn [16] and soil samples. The mechanism of photodegradation is thoroughly revealed [16, 17] and the photodegradation products are well defined and identified. The photodegradation of atrazine and prometryn results in compounds with more polar character. The above mentioned column chromatographic investigation of the photodegradation products showed good correlation with these findings. The photodegradation products of atrazine and prometryn bind stronger to both soil samples. Degradation products with free amino-groups have more polar character compared with the original pesticides. The bond strength was found to be the highest in the case of 2,4-diamino-1,3,5-triazine, even applying 500mL chloroform as eluent was not enough to wash off this product from the column.

We plan to continue the research on the pesticide-soil interactions. As a continuation of this work we plan to study thoroughly the adsorption of the photodegradation products of other pesticides in different soils.

4. Conclusion

We investigated the soil pesticide interactions between two type of soils and some distinctive pesticides and photodegradation products. Brown forest soil binds apolar pesticides stronger than sandy soil, binding force of bound substances is increasing with depth. Chemically similar triazine type herbicides have similar adsorption characteristics compared with a more polar compound (diuron). The photodegradation products of atrazine and prometryn bind stronger to soil particles than the original pesticide molecules. We created the „relative adsorption value” to evaluate binding force of the same compound in sandy and brown forest soil.

5. Acknowledgements

The authors thank the Hungarian National Science Foundation (Grant OTKA: F 34714) for financial support of this work.

6. References

[1.] P. C. Wilson, S. B. Wilson, P. J. Stoffella, Compost Sci. Util. 11(4) (2003) 282.
[2.] C. Vandervoort, M. J. Zabik, B. Branham, D. W. Lickfeldt, B. Environ. Contam. Tox. 58(1) (1997) 38.
[3.] R. A. Haugland, D. J. Schlemm, R. P. Lyons, P. R. Sferra, A. M. Chakrabarty, Appl. Environ. Microbiol. 56(5) (1990) 1357.
[4.] K. D. Racke, C. R. Frink, B. Environ. Contam. Tox. 42(4) (1989) 526.

[5.] J. J. Aaron, M. A. Oturan, Turk. J. Chem. 25 (2001) 509.
[6.] Coly, J. J. Aaron, Talanta 41 (1994) 1475.
[7.] L. Muszkat, L. Feigelson, L. Bir, K. A. Muszkat, Pest Manag. Sci. 58(11) (2002) 1143.
[8.] T. W. Jones, W. M. Kemp, J. C. Stevenson, J. C. Means, J. Environ. Qual. 11 (1982) 632.
[9.] F. Gianturco, C. M. Chiodaroli, I. R. Bellobono, M. L. Raimondi, A. Moroni, B. Gawlik, Fresen. Environ. Bull. 6 (1997) 461.
[10.] S. Chen, M. Zhao, Y. Tao, Microchem. J. 54(1) (1996) 54.
[11.] U. Dörfler, E. A. Feicht, I. Scheunert, Chemosphere 35 (1997) 99.
[12.] W. F. Ritter, R. W. Scarborough, A. E. M. Chirnside, J. Contam. Hydrol. 15 (1994) 73.
[13.] R. S. Kookana, H. J. Di, L. A. G. Aylmore, Aust. J. Soil. Res. 33(6) (1995) 1019.
[14.] H. J. Di, L. A. G. Aylmore, R. S. Kookana, Soil Sci. 163(5) (1998) 404.
[15.] G. K. Sims, A. M. Cupples, Pestic. Sci. 55(5) (1999) 598.
[16.] Kiss, Z. Naár, S. Rapi, NATO ASI Series, Suppl. 23/98 (2004) 125.
[17.] Kiss, Cs. Csutorás, D. Virág, Euroanalysis XIII., Salamanca, Spain, 05-10 September, (2004).